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REDUCTION OF CHLORIDE SALTS IN AUSTEMPERING QUENCH BATHS

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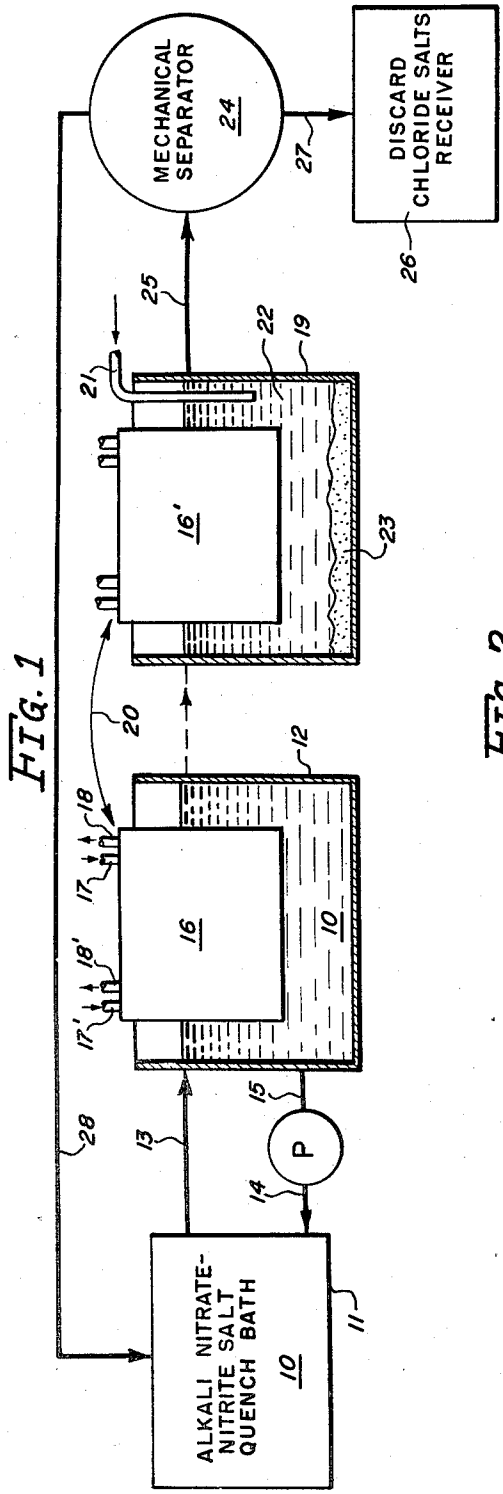


FIG. 1

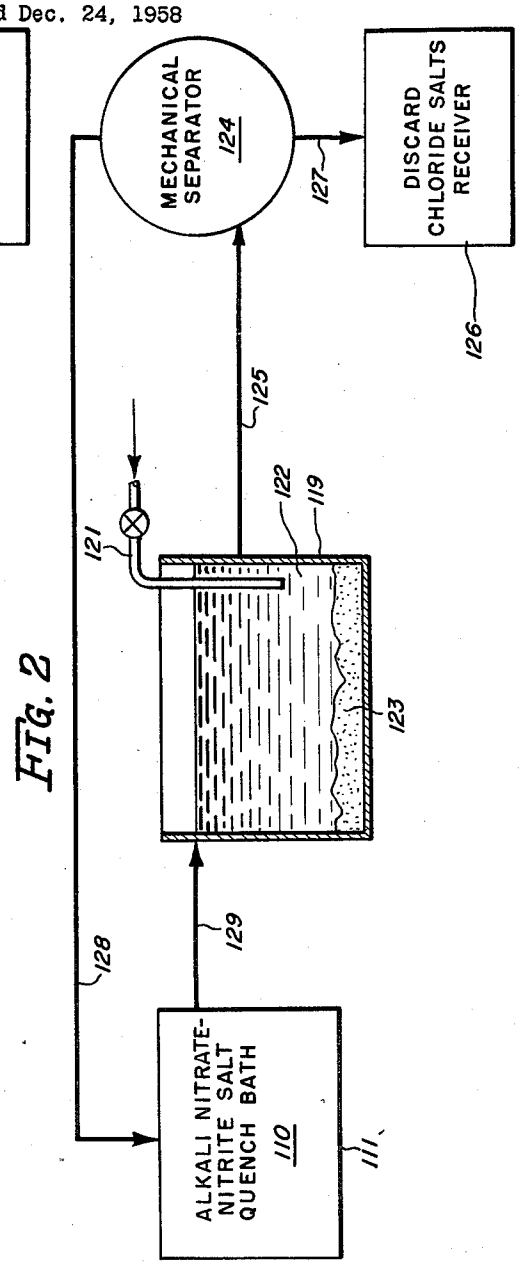


FIG. 2

INVENTORS
John A. Halgren
Edward A. Solecki
Robert H. Pinkel

ATTORNEY

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REDUCTION OF CHLORIDE SALTS IN AUSTEMPERING QUENCH BATHS

John A. Halgren, Downers Grove, and Edward A. Solecki and Robert H. Pinkel, Chicago, Ill., assignors to International Harvester Company, Chicago, Ill., a corporation of New Jersey

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9 Claims. (Cl. 148—28)

This invention relates to a method for preventing the increase in concentration of inorganic chloride salts in a molten nitrate-nitrite salt quench bath beyond a tolerable limit. More in particular this invention relates to a method of economically removing excess inorganic chloride salts from an inorganic molten nitrate-nitrite salt bath, used for quenching of steel articles, commonly referred to as austempering or martempering.

In one process of austempering a steel article, the article is immersed in an austenitizing bath of molten alkali metal chlorides at about 1600° F. for a specified period of time. A commonly used commercial chloride austenitizing bath for such purpose may consist of a mixture containing about 50% sodium chloride and about 50% potassium chloride. After the immersion time of the article in the fused chloride mixture has elapsed, the article is removed from the chloride austenitizing bath and immediately immersed in an austempering quench bath. The austempering quench bath initially may consist of a mixture of about 20% sodium nitrate, 52% potassium nitrate, and about 28% sodium nitrite maintained at a temperature of about 750° F. After immersion in the austempering quench bath for a specified period of time the article is removed, cooled and rinsed free of adhering salts. Further treatment of the article is according to conventional methods which form no part of the present invention and will therefore not be further considered.

When the article is transferred from the chloride austenitizing bath to the austempering quench bath, some of the chloride salts physically adhere to the article, are deposited in the quench bath when the article is immersed therein, and go into solution. From this it can be appreciated that with repeated austempering operations with successive steel articles in the same baths, the concentration of chloride salts in the quench bath gradually increases. Since the melting point of the initial nitrate-nitrite quench bath is in the order of about 300° F., while that of the chlorides is about 1300° F., the chloride content of the quench bath will increase until it reaches its limit of solubility in the nitrate-nitrite bath, after which additional chlorides will precipitate out and settle to the bottom of the bath or will freeze against colder surfaces within the bath. As it is desirable to maintain the quench bath at about 750° F., it becomes obvious that the bath will become contaminated to the point where it will be completely unsuable and could even freeze at this temperature if the chloride content becomes sufficiently high. It has been found that the quench bath at 750° F. can tolerate the presence of chloride salts up to about 17% by weight as a maximum concentration. Thus if the chloride content exceeds about 17% by weight, the chlorides precipitate out, forming a sludge in the quench bath. At this point the quench salts are either (1) completely or partly discarded and replaced by fresh nitrate-nitrite salts or (2) the sludge is manually bailed out by means of a screened shovel which allows the nitrate-nitrite salts to pass through but retains the precipitated chlorides. Because of wetting action, the sludge which

is discarded may contain up to 70% nitrate-nitrite salts and only 30% chloride salts. However, such procedure is not desirable because sodium nitrate, potassium nitrate and sodium nitrite salts are much more expensive than the chloride salts which are comparatively cheap. Thus the problem is to remove the chloride salts from the quench bath with minimal loss of nitrate-nitrite salts for maintaining fused condition of the quench bath at its operating temperature, thereby reducing the cost of the austempering operation.

It is therefore an object of this invention to separate inorganic alkali metal chlorides from a molten alkali nitrate-nitrite salt quench bath.

A further object of this invention is to recover economically a major portion of the sodium nitrate-potassium nitrate-sodium nitrite salts from an austempering and martempering quench bath for re-use in said bath.

A still further object of this invention is to reclaim economically the sodium nitrate-potassium nitrate-sodium nitrite salts of an austempering and martempering quench bath for re-use in said bath by removing the major portion of chloride salts therefrom.

Another object of this invention is to economically remove sufficient chloride salts from an austempering and martempering quench bath to maintain the freezing temperature of said bath substantially below its desired operating temperature.

Another object is to maintain the chloride content of the quench bath both low and constant so that the quenching power of the bath is stabilized at an efficient nitrate-nitrite composition.

These and other desirable and important objects inherent in and encompassed by the invention will be more readily understood from the ensuing description, the appended claims and the annexed drawings wherein:

Figure 1 is a diagram illustrating schematically the components comprising the apparatus and their respective relationship to the invention.

Figure 2 is a diagram illustrating schematically the components comprising the apparatus and their respective relationship to each other in a modified form of the invention.

As mentioned previously in repeated austempering and martempering operations, by mechanical adherence to the articles being austenitized in the alkali metal chloride bath (not shown), chloride salts are mechanically deposited in the austempering and martempering quench bath **10** (Figure 1), and after a time the build-up of chloride salt content in the bath **10** would reach a concentration such that the bath **10** would no longer remain fluid at the desired quenching temperature. When the chloride content exceeds its solubility at the operating temperature of the bath, freezing begins on the walls of the receptacle **11** supporting the bath **10** and progresses inwardly until the bath is completely sludged over, and/or the excess chlorides are precipitated within the bath **10** and settle to the bottom of the tank until the bath is completely inoperable for its intended purpose. This can be avoided as follows:

Referring to Figure 1 there is provided a plate separator pot **12** communicatively connected to the bath **10** by a pipe indicated at **13** on the upper portion thereof. The lower portion of the bath **10** is communicatively connected to the outlet side of a pump P by a pipe indicated at **14**. The inlet side of the pump P is communicatively connected to the pot **12** by the pipe indicated at **15**. Thus the pump P functions to circulate the liquid salts of the bath **10** through the pot **12**. The tempertaure in pot **12** is maintained at or above the operating temperature of bath **10**. The pot **12** is provided with a removable separator plate **16** partly immersed therein. The plate **16** is provided with conventional passages (not shown) for circulating a fluid coolant therethrough. The

liquid coolant enters the plate **16** at the inlet ports **17** and **17'** and is discharged through the outlet ports **18** and **18'** as shown in Figure 1. In order to prevent an appreciable temperature reduction of the pot **12** it is preferred that the coolant be adjusted to maintain the plate **16** at about 100° F. below the temperature of pot **12**. Thus the plate **16** being about 100° F. cooler than the pot **12** causes the chloride salts to adhere and crystallize out in solid form on the plate **16**. When the plate **16** contains an appreciable amount of adhered chloride salts the entire plate **16** is mechanically removed from the pot **12** and partly immersed (to the same extent as that in the pot **12**) into a low temperature or quench pot **19** as indicated schematically by the arrow **20**. For convenience when the plate **16** is removed from the separator pot **12** to the low temperature or quench pot **19** it is referred to by the numeral **16'**.

The quench pot **19** contains a liquid solution **22** of about 87% by weight of nitrate-nitrite salts with about 10% water and up to about 3% chloride salts. With reference to chloride salts (potassium chloride and sodium chloride) this composition at 3% chloride salt corresponds to the maximum solubiilty of the chloride salts in such a bath. The quench pot **19** is maintained at a temperature of between 275° F. and 325° F., preferably at about 300° F. In order to provide water to form the above mentioned solution which also serves to control the temperature in the quench pot **19** a water inlet pipe **21** is provided which may or may not extend below the surface of the liquid in the quench pot **19**. The water entering the pipe **21** may conveniently be the rinse water obtained when rinsing the quenched article which may contain some nitrate-nitrite salts as well as chlorides. Thus the nitrate-nitrite salts may be recovered in a simultaneous operation.

When the plate **16** is mechanically removed from the pot **12** the salts adhered thereto consists of a sludge containing about 60% chloride salts in solid form and the remainder is essentially liquid nitrate-nitrite salts mechanically occluded with the solid chlorides. As soon as the plate **16** is immersed as **16'** in the quench pot **19**, the sludge loses its adherence to the plate **16'** apparently due to the temperature gradient between the plate and the solution **22** and the increased solubility of the nitrate-nitrite salts in solution **22** because of the water therein. The chlorides precipitate while solution **22** is maintained essentially unchanged by adding water to keep an amount of about 10% water in the bath. Although the chloride precipitate in the quench pot **19** is indicated as settling on the bottom of the quench pot as indicated at **23**, what really takes place is that a slurry is formed in the quench pot wherein the liquid phase is solution **22** and the solid phase is a mixture of potassium chloride and sodium chloride. Thus the slurry comprises the solution **22** and the precipitated chloride salts **23**. The slurry **22, 23** is drawn from the quench pot **19** into a mechanical separator **24** through the communicating pipe **25** which may be by gravity or a pump (not shown) interposed in the pipe **25**. The mechanical separator **24** may comprise a conventional unit such as a filter press or centrifuge. The solids removed by the separator **24** are deposited into the receiver **26** through pipe **27** and comprise mainly chloride salts with whatever small amount of solution **22** which may adhere after mechanical separation and subsequent rinsing processes. The remainder of the solution **22**, containing about 87% by weight of nitrate-nitrite salts, 10% water and about 3% chloride salts, discharged from the mechanical separator **24** is deposited either directly or after being reheated to remove the water in the austempering quench bath **10** through the pipe **28** by means of gravity or a pump (not shown) interposed therein. It also could be cast into bars, allowed to freeze, and then added to the bath **10**.

Replenishment of the solution **22** in the quench pot **19** is from the water introduced through the pipe **21**, and the nitrate-nitrite salts occluded in the adhered chloride salts carried over mechanically from the separator pot **12** to the quench pot **19** on the separator plate **16** and **16'**. As pointed out previously the salt deposit on the plate **16** consists of about 60% chloride salts and about 40% mechanically occluded liquid nitrate-nitrite salts.

The salts delivered to the receiver **26** containing mostly chloride salts and the balance nitrate-nitrite salts are discarded if it is not practical from an economical point of view to subject this material to a further extraction process.

From the above it has been shown a practical and economical method of reclaiming in excess of 80% of the nitrate-nitrite salts which can be effectively re-cycled back to the austempering quench bath **10**.

Figure 2 shows a modified form of the invention wherein the separator plate **16** and **16'** and the plate separator pot **12** are eliminated and yet comparable results can be obtained with that described previously. For clarity the components employed in the modified form of the invention which are similar to that of Figure 1 are designated by like numerals except that each is increased by 100. Thus the alkali nitrate-nitrite salt quench bath **110** is formed by walls **111**. The fused salts of the bath **110** flow directly into the low temperature pot **119** by gravity or other suitable means through pipe **129** as illustrated in Figure 2. The low temperature pot **119** contains a liquid solution **122** consisting of about 87% by weight of sodium nitrate-potassium nitrate-sodium nitrite salts, about 10% water and about 3% alkali metal chlorides and is maintained at about 300° F. as before. To assist in cooling and maintaining the liquid **122** at 300° F. temperature as well as keeping the water content at about 10% by weight a water inlet pipe **121** is provided. The discharge end of the pipe **121** may or may not be positioned below the surface of solution **122** in the low temperature pot **119**.

As the fluid salts from the bath **110** enter the pot **119** through the pipe **129** the reduction in temperature from the operating temperature to 300° F., causes the chloride salts which are in excess of their limit of solubility in solution **122** to crystallize out in solid form **123**. Although the drawing indicates that the solid chlorides **123** settle at the bottom of the pot **119** what actually happens is that, as before, a slurry is formed. The slurry **122, 123** comprises the solution **122** as the liquid phase and the excess solid chloride salts as the solid phase. The slurry **122, 123** thus formed is drawn off to the mechanical separator **124**. Again the mechanical separator may comprise a conventional unit such as a filter press or centrifuge. The solids removed by the separator **124** are deposited into the receiver **126** through pipe **127** and comprise mostly chloride salts with whatever small amount of solution **22** which adheres after mechanical separation and subsequent rinsing processes. The remainder of the solution **122** containing about 87% by weight of nitrate-nitrite salts, 10% water and about 3% chloride salts, discharged from the separator **124** is deposited in the austempering quench bath **10** through the pipe **128** in the same manner as previously described.

In order to recover the nitrate-nitrite salts which physically adhere to the steel articles being processed after the articles are removed from bath **110**, the water from the bath (not shown) in which they are rinsed is introduced through inlets **21** or **121** into baths **19** and **119**, thus recovering the nitrate-nitrite salts which dissolved in the rinse bath.

Having thus described the preferred embodiments of the invention it can now be seen that the objects of the invention have been fully achieved and it must be understood that changes and modifications may be made which do not depart from the spirit of the invention nor from the scope thereof as defined in the appended claims.

What is claimed:

1. For reducing contaminating excess alkali metal chlorides content of a molten austempering and martempering quench bath initially containing salts selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method of flowing said contaminated molten bath into a low temperature pot, introducing into said pot up to about 10% by weight of water to form a liquid solution with said salts for precipitating excess alkali metal chlorides in solid phase, and mechanically separating said solid phase alkali metal chlorides from said liquid composition.

2. For removing substantially all contaminating alkali metal chlorides in excess of about 3 percent by weight from a molten austempering and martempering quench bath initially containing salts selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method of transferring at least a portion of said contaminated molten bath into a low temperature pot, introducing into said pot up to about 10% by weight of water to form a liquid phase composition with said salts for precipitating excess alkali metal chlorides in solid phase, mechanically separating said solid phase alkali metal chlorides substantially from said liquid phase composition, and discharging said liquid phase composition into said bath.

3. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing salts selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method of transferring at least a portion of said contaminated bath into a low temperature pot, adding to said pot sufficient water to form a liquid phase composition with said salts for precipitating excess alkali metal chlorides in solid phase, mechanically separating said solid phase alkali metal chlorides substantially from said liquid phase composition and discharging said liquid phase composition into said bath.

4. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing salts selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method of transferring at least a portion of said contaminated bath into a low temperature pot, said pot being maintained at a temperature between about 275° F. and about 325° F., introducing into said pot sufficient water to form a liquid phase composition with said salts for precipitating excess alkali metal chlorides in solid phase, mechanically separating said solid phase alkali metal chlorides substantially from said liquid phase composition and discharging said liquid phase composition into said bath.

5. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing at least one salt selected from the group consisting of sodium nitrate, potassium nitrate, and sodium nitrite, the method of transferring at least a portion of said contaminated bath into a low temperature pot, said pot being maintained at a temperature of about 300° F., introducing into said pot sufficient water to form a liquid phase composition consisting of about 10% by weight of water, up to about 3% by weight of alkali metal chlorides and the balance being said nitrogen containing salts for precipitating alkali metal chlorides in excess of said 3% by weight in solid phase, mechanically separating said solid phase alkali metal chlorides substantially from said liquid phase composition and discharging said liquid phase composition into said bath.

6. For reducing contaminating alkali metal chlorides content of a molten austempering and martempering quench bath initially containing at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method comprising the flowing of said contaminated molten bath into a separator pot, providing a plate, means for maintaining the temperature of said plate substantially below the temperature of said bath, providing a low temperature pot, said low temperature pot having a liquid solution comprising of up to about 3 percent by weight alkali metal chlorides with water and at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, said liquid solution being maintained at a temperature substantially below the temperature of said plate, immersing at least a portion of said plate in said separator pot for inducing at least a part of said chlorides of said bath to precipitate in solid phase on said plate, mechanically removing from said separator pot, said plate with said precipitated chlorides adhered thereto and thereafter immersing at least a portion of said plate with said solid phase chlorides into said liquid solution in said low temperature pot for depositing said solid phase chlorides therein, mechanically extracting said solid phase chlorides from said liquid solution and returning said extracted liquid solution to said austempering and martempering quench bath.

7. For removing substantially all contaminating alkali metal chlorides in excess of about 3 percent by weight from a molten austempering and martempering quench bath initially containing at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method comprising the transferring of said contaminating molten bath into a separator pot, providing a plate, means for maintaining the temperature of said plate approximately 100° F. below the temperature of said separator pot, providing a low temperature pot, said low temperature pot having a liquid solution comprising of up to about 3% by weight of alkali metal chlorides with about 10% by weight of water and the balance being at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, said liquid solution being maintained at a temperature of about 275° F., to about 325° F., immersing at least a portion of said plate in said separator pot for inducing at least a part of said chlorides of said bath to precipitate in solid phase on said plate, mechanically removing said plate with said precipitated chlorides adhered thereto and thereafter immersing at least a portion of said plate with said solid phase chloride salts into said liquid solution in said low temperature pot for depositing said solid phase chlorides therein, mechanically extracting said solid chlorides substantially from said liquid solution and returning said extracted liquid solution to said austempering and martempering bath.

8. For removing substantially all contaminating alkali metal chlorides in excess of about 3 percent by weight from a molten austempering and martempering quench bath initially containing at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method comprising the transferring of at least a portion of said contaminated bath into a separator pot, providing a plate, means for maintaining the temperature of said plate approximately 100° F. below the temperature of said separator pot, providing a low temperature pot, said low temperature pot containing a liquid solution comprising of up to about 3 percent by weight of alkali metal chlorides with water and the balance being at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, means for introducing into and maintaining about 10 percent by weight of water in said liquid solution, said liquid solution being maintained at a temperature of about 275° F., to about 325° F., immersing at least a portion of said plate in said separator pot for inducing at least a part of said chlorides of said bath to precipitate in solid phase on said plate, mechanically removing said plate with said precipitated chlorides adhered thereto and thereafter immersing at least a portion of said

plate with said solid phase chlorides into said liquid solution in said low temperature pot for depositing said solid phase chlorides therein, mechanically extracting said solid chlorides substantially from said liquid solution and returning said extracted liquid solution to said austempering and martempering bath.

9. For removing substantially all contaminating alkali metal chloride salts in excess of about 3 percent by weight from a molten austempering and martempering quench bath initially containing at least one salt selected from the group consisting of sodium nitrate, potassium nitrate, and sodium nitrite, the method comprising the transferring of at least a portion of said contaminated bath into a separator pot, providing a plate, means for maintaining the temperature of said plate at approximately 100° F., below the temperature of said pot, providing a low temperature pot, said low temperature pot containing a liquid solution comprising of up to about 3% by weight of alkali metal chlorides with water and the balance being

at least one salt selected from the group consisting of sodium nitrate, potassum nitrate, and sodium nitrite, means for introducing into and maintaining about 10 percent by weight of water in said liquid solution, said liquid solution being maintained at a temperature of about 275° F., to about 325° F., immersing at least a portion of said plate in said separator pot for inducing at least a part of said chloride of said bath in excess of about 3 percent by weight to preciptate in solid phase on said plate, mechanically removing said plate with said precipitated chlorides adhered thereto and thereafter immersing at least a portion of said plate with said solid phase chloride salts into said liquid solution in said low temperature pot for depositing said solid phase chlorides therein, mechanically extracting said solid chlorides substantially from said liquid solution and returning said extracted liquid solution to said austempering and martempering bath.

No references cited.